



# Effect of microwaves, ultrasounds and interlayer anion on the hydrocalumites synthesis



Judith Granados-Reyes, Pilar Salagre, Yolanda Cesteros\*

Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, C/Marcel·lí Domingo s/n, 43007 Tarragona, Spain

## ARTICLE INFO

### Article history:

Received 5 January 2014  
Received in revised form 31 July 2014  
Accepted 2 August 2014  
Available online 12 August 2014

### Keywords:

Hydrocalumite  
Microwaves  
Ultrasounds  
Refluxing  
Autoclave

## ABSTRACT

Several hydrocalumites were precipitated from nitrate or chloride salts with and without ultrasounds, and aged hydrothermally in autoclave or by refluxing with and without microwaves. The use of ultrasounds during coprecipitation led to more crystalline hydrocalumites whereas the use of autoclave and microwaves during aging, favoured the formation of a secondary phase, katoite, in addition to hydrocalumite. The presence of katoite affected the crystallization of hydrocalumite. Hydrocalumites with nitrates as interlayer anions were slightly less crystalline than those prepared with chloride anions. Additionally, the synthesis with nitrates resulted in the formation of higher amounts of katoite in autoclave conditions. Hydrocalumites exhibited thin regular hexagonal layers, as observed by SEM and TEM, with lower particle size for the samples aged with microwaves. Interestingly, the hydrocalumite prepared from nitrates by coprecipitation in ultrasounds and aged under microwaves resulted in the highest surface area measured ( $25 \text{ m}^2/\text{g}$ ) according to the additional mesoporosity observed by  $\text{N}_2$  physisorption.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

Hydrocalumite-type compounds (HC) belong to the layered double hydroxides (LDH) family. LDHs are anionic clays with general formula  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2][\text{X}^{q-}_{x/q} \cdot n\text{H}_2\text{O}]$  where  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]$  cation represents the layer composition, and  $[\text{X}^{q-}_{x/q} \cdot n\text{H}_2\text{O}]$  the interlayer composition. In the particular case of hydrocalumites, the layers are formed by  $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$  whereas the interlayers are composed of water molecules and anions (e.g.  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , or  $\text{Cl}^-$ ) [1–9]. For hydrocalumite,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ , fixed in a molar ratio of two, are seven and sixfold coordinated, respectively, being the seventh ligand of the Ca-polyhedron a water molecule from the interlayer [5]. Hydrocalumites have been extensively used in the immobilization of toxic cations [4–11], the optimization of concrete properties [2,3,12–14], and, in less extent, for catalysis due to their basic properties [15]. The structure of hydrocalumites collapses at temperatures between 400 and 600 °C due to the dehydroxylation of their octahedral layers, giving rise to the formation of an amorphous, basic Ca–Al mixed oxide,  $\text{Ca}(\text{Al})\text{O}_x$ , which may be also used as catalyst for organic reactions such as the Meerwein–Ponndorf–Verley reaction [16], the isomerization of 1-butene [17] or the transesterification of castor bean oil and methanol [18].

In the existing literature, hydrocalumites are usually prepared by the co-precipitation of calcium and aluminium salts (typically chlorides or nitrates) with NaOH at controlled pH in an inert atmosphere, to avoid the presence of carbonates, and with temperature (60–80 °C), using conventional heating. Then, the coprecipitated gel is aged by refluxing at temperatures between 60 and 80 °C for long times (24–48 h) [6,15,19]. On the other hand, for the preparation of  $\text{OH}^-$  containing hydrocalumites, a direct method based on the controlled hydrolysis of  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  alkoxides has been reported [16]. Other hydrocalumites preparation methods are the sol–gel methods and the homogeneous precipitation with urea [15].

In recent years, the use of microwaves for the synthesis or modification of materials is becoming an important tool to decrease the synthesis time, with the subsequent energy saving, and to modify the sample properties, which can be of interest for catalysis [20–24]. Additionally, ultrasounds is another interesting technique to improve the synthesis of materials since, when used for the mixing of reagents, allows obtaining materials with more homogeneous composition [23–25]. In a previous work, we synthesized hydrocalumites from chloride salts faster by using microwaves during the aging treatment (3 h) than by conventional heating (24 h) [26].

The aim of this work was to study the effect of using ultrasounds during the coprecipitation step, and microwaves during the aging treatment of several hydrocalumites, on their surface and basic properties. Hydrocalumites were synthesized from

\* Corresponding author. Tel.: +34 977558785; fax: +34 977559563.  
E-mail address: [yolanda.cesteros@urv.cat](mailto:yolanda.cesteros@urv.cat) (Y. Cesteros).

nitrate or chloride salts, and during the aging treatment autoclave or refluxing conditions were used. Several hydrocalumites were also prepared by conventional heating (with and without ultrasounds) for comparison.

## 2. Experimental

### 2.1. Samples preparation

Two series of hydrocalumites were synthesized by the co-precipitation method from different starting salts, chlorides (serie HC1) or nitrates (serie HC2), at 60 °C under vigorous magnetic stirring using deionized/decarbonated water as well as nitrogen atmosphere. In a typical synthesis, two different aqueous solutions containing  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (Sigma–Aldrich) and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (Riedel-de Haën) or  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Sigma–Aldrich) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Sigma–Aldrich) were prepared with a 2:1 molar ratio of  $\text{Ca}^{2+}/\text{Al}^{3+}$ . The solutions were added dropwise to a 500 ml four neck round-bottom flask in an oil bath at 65 °C previously filled with 250 ml of a mixture of water/ethanol in a 2:3 volumetric ratio. The pH was kept constant at  $11.5 \pm 0.1$ , by the simultaneous addition of an aqueous solution of 2 M NaOH (Panreac). After complete addition of the metallic salts, the two mother solutions were aged by several treatments.

Four samples were aged under refluxing, two at 60 °C for 24 h under conventional heating (HC1R<sub>24</sub> and HC2R<sub>24</sub>) and the other two using microwave irradiation (Milestone ETHOS-TOUCH CONTROL) at 60 °C for 6 h (HC1RM<sub>w6</sub> and HC2RM<sub>w6</sub>). Other six samples were prepared using an autoclave. Two of them were aged in an oven at 180 °C for 1 h (HC1AC<sub>1</sub> and HC2AC<sub>1</sub>) and other four were aged in a microwave oven at 180 °C for 1 and 3 h (HC1AM<sub>w1</sub>, HC1AM<sub>w3</sub>, HC2AM<sub>w1</sub> and HC2AM<sub>w3</sub>). Two more samples were prepared by aging the mother solution obtained from the coprecipitation of the nitrate salts in autoclave by conventional heating and with microwaves at 100 °C for 1 h (HC2AC100 and HC2AM<sub>w100</sub>).

Finally, four hydrocalumites were prepared by co-precipitation of chlorides salts and nitrates salts in the same conditions than those commented above, but using ultrasounds instead of magnetic stirring during coprecipitation. The ultrasound device was heated until 60 °C. Once reached the temperature, we started the precipitation of salts under ultrasounds stirring, inert atmosphere and pH constant of 11.5. After coprecipitation, two samples were aged by refluxing under conventional heating at 60 °C for 24 h (HC1USR<sub>24</sub>, HC2USR<sub>24</sub>) and two more were aged by refluxing with microwaves at 60 °C for 6 h (HC1USM<sub>w6</sub>, HC2USM<sub>w6</sub>).

All samples were filtered at room temperature, washed with deionized water and then dried in an oven at 80 °C overnight. Table 1 summarizes the preparation conditions used.

### 2.2. X-ray diffraction (XRD)

Powder X-ray diffraction patterns of the samples were obtained with a Siemens D5000 diffractometer using nickel-filtered  $\text{CuK}\alpha$  radiation and detecting between  $2\theta$  values of 5°–70°. Crystalline phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files (035-0105 – Calcium aluminium hydroxide chloride hydrate –  $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ , 089-6723 – Calcium Aluminium Nitrate Hydroxide Hydrate –  $\text{Ca}_2\text{Al}(\text{OH})_6\text{NO}_3 \cdot 2\text{H}_2\text{O}$  and 089-0217 – Katoite –  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ ).

Cell parameter  $c$  was calculated from (006) for hydrocalumites type chlorides and (002) for hydrocalumites type nitrates whereas cell parameter  $a$  was calculated from (110) for both. The Rietveld method was used to perform quantitative phase analysis of multi-component mixtures from the X-ray powder diffraction data. To apply this method it is only necessary to know the crystal structure of each phase of interest [27].

### 2.3. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-OES)

Elemental analysis of the samples was obtained with an ICP-OES analyser (Induced Coupled Plasma-Optical Emission Spectroscopy) from Spectro Arcos. The digestion of all hydrocalumites was carried out with concentrated  $\text{HNO}_3$ . Analyses were performed by triplicate.

### 2.4. Scanning electron microscopy (SEM)

Scanning electron micrographs were obtained with a JEOL JSM-35 C scanning microscope operating at an accelerating voltage in the range 15–30 kV, work distance of 14 mm and magnification values between 5000 and 30,000×.

### 2.5. Transmission electron microscopy (TEM)

Transmission electron microscopy of the samples was performed using a JEOL electron microscope Model 1011 with an operating voltage of 80 kV. Samples were dispersed in acetone and a drop of the suspension was poured on to a carbon coated copper grid and dried at room temperature before measurements. The magnification values used were between 20 and 100 k.

**Table 1**  
Aging treatments of hydrocalumites.

Sample	Ultrasounds during coprecipitation	Heating during aging	Technique during aging	Aging temperature (°C)	Aging time (h)
HC1R <sub>24</sub>	No	Conventional	Refluxing	60	24
HC1RM <sub>w6</sub>	No	Microwaves	Refluxing	60	6
HC1AC <sub>1</sub>	No	Conventional	Autoclave	180	1
HC1AM <sub>w1</sub>	No	Microwaves	Autoclave	180	1
HC1AM <sub>w3</sub>	No	Microwaves	Autoclave	180	3
HC1USR <sub>24</sub>	Yes	Conventional	Refluxing	60	24
HC1USRM <sub>w6</sub>	Yes	Microwaves	Refluxing	60	6
HC2R <sub>24</sub>	No	Conventional	Refluxing	60	24
HC2RM <sub>w6</sub>	No	Microwaves	Refluxing	60	6
HC2AC <sub>1</sub>	No	Conventional	Autoclave	180	1
HC2AM <sub>w1</sub>	No	Microwaves	Autoclave	180	1
HC2AM <sub>w3</sub>	No	Microwaves	Autoclave	180	3
HC2AC100	No	Conventional	Autoclave	100	1
HC2AM <sub>w100</sub>	No	Microwaves	Autoclave	100	1
HC2USR <sub>24</sub>	Yes	Conventional	Refluxing	60	24
HC2USRM <sub>w6</sub>	Yes	Microwaves	Refluxing	60	6

Download English Version:

<https://daneshyari.com/en/article/72979>

Download Persian Version:

<https://daneshyari.com/article/72979>

[Daneshyari.com](https://daneshyari.com)